

JAPANESE PATENT OFFICE
PATENT DISCLOSURE BULLETIN

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1. Title of the Invention

Catalyst for methanol improvement.

Claim

(1) Catalyst for the improvement of methanol characterized by treating copper-nickel-zinc alloy in an alkaline solution which contains Raney catalyst consisting of copper, nickel and zinc.

Details of the Invention

Utility to the industry: This invention is about the methanol-improving catalyst. To be more specific, it is about the methanol-improving catalyst which is suitable for use in the making of hydrogen and carbon monooxide selectively from methanol.

Conventional technics and their problems: Usually fuels for internal combustion engines and as the starting materials for the production of reducing gases crude oil or petroleum from crude oil is used.

However, with recent rise in the price of crude oil there is trend of multiple uses of crude oil. Particularly methanol, which can be made not only from coal or natural gas but can also be made much cheaper than naphtha but also can be improved to make hydrogen and carbon monooxide so as the energy source it can be used from the waste energy source. Besides, it does not contain sulfur compounds like naphtha so it attracts lots of attention as the excellent source for the production of high purity reducing gas.

In the past, as the catalyst for the improvement of methanol there are various proposals such as attachment of platinum group element(s) on a carrier like alumina (Japanese Patent Disclosure No. Sho 60-82138, Sho 59-199043, Sho 58-174237) or alloys consisting of base metals of copper, nickel, chromium or zinc or their oxides (Japanese Patent Disclosures Sho 58-216742, Sho 57-174138, Sho 57-174139) but these catalysts all have low activity at low tem-

perature. They also have low selectivity for hydrogen or carbon monooxide and tend to deteriorate under heat. Besides, their preparations are complicated.

Objective of the invention: This invention is to offer methanol-improving catalysts which have excellent activity at low temperatures, good selectivity for hydrogen or carbon monooxide and will not deteriorate for long period of time.

Means to achieve the said objectives: The inventors studied intensively to achieve the said goals and found that certain type of catalysts containing specific Raney catalyst have high activity compared with the conventional catalysts with oxides and also will not deteriorate for long period of time and yet still have high selectivity for hydrogen or carbon monooxide and thus came up with this invention.

In summary the catalyst is prepared by treating the copper-nickel-zinc alloy in alkaline solution so it will contain a Raney catalyst containing copper-nickel-zinc.

Contents of copper, nickel and zinc in the said copper-nickel-zinc alloy are: copper, 5-30 weight %; nickel, 5-50 weight % and zinc, 30-90 weight %.

According to this invention, by treating this kind of alloy in an alkaline solution the catalytically inactive zinc is activated. The amount of zinc eluted is usually 10-90 weight % of zinc in the original alloy. The treatment is usually done in aqueous solution of either sodium hydroxide, potassium hydroxide or potassium carbonate at 20-100 °C.

Contents of copper, nickel and zinc in the alloy after the treatment are: copper, 10-50 weight %; nickel, 20-80 weight % and zinc, 10-60 weight %. When the contents of copper and nickel are below the said levels activity of the resultant catalyst may be lower while if higher the formation of methane may become difficult which may reduce selectivity of hydrogen or carbon monooxide. Also, if the content of zinc is below 10 weight % the effect of zinc will be less which will affect selectivity to hydrogen or carbon monooxide while if over 60 weight % the surface area will be decrease and may lead to lower catalytic activity.

The said catalyst can be prepared by the treatments such as separation-water wash-drying-molding-reduction.

Separation can be done either by filtration, centrifugation, decantation or other methods commonly used.

Water wash can be done with distilled water or deionized water for the removal of the said

alkaline solution till it is near pH 7.

Drying can be done by air drying in 3-12 hours.

In the molding can be done by press molding or punching after a lubricant like graphite is added to the treated alloy to make pellets, granules, flakes or plates.

Reduction can be usually done in hydrogen and/or carbon monoxide atmosphere at 200-500 °C. A inert gas can also be used. The said inert gas can be argon, helium, neon or nitrogen, etc.

When such a catalyst is used in the improvement of methanol the following conditions can be used. Temperature is usually at 200-800 °C, preferably 300-400 °C. Pressure is usually 0-20 Kg/cm²G, preferably 0-10 Kg/cm²G. If the temperature is below 200 °C not enough catalytic activity can be obtained. On the other hand, if it is higher than 800 °C catalytic activity will decline.

Rate of methanol feeding is usually 0.1-20 hr⁻¹ LHSV (liquid space flow rate), preferably 1-10 hr⁻¹. When LHSV is less than 0.1 hr⁻¹ the reaction may not proceed thoroughly. On the other hand if it is higher than 10 hr⁻¹ no better result can be obtained.

The catalyst thus prepared can be used in the preparation of hydrogen used in fuel batteries or as the reducing gas in the preparation of semiconductors or carbon monoxide used as fuel in internal combustion engines or power generating boilers by improving methanol.

Benefit from this invention: Unlike conventional catalysts for methanol improvement the catalyst from this invention does not use oxides as the catalyst components. Therefore it brings in the following benefits:

- (1) It has activity in wide temperature range and does not deteriorate for long time.
 - (2) It has high selectivity for hydrogen and carbon monoxide.
 - (3) Improvement of methanol can be done efficiently.
 - (4) Waste energy can be used in the reaction and highly pure reducing gas can be made.
- Thus, it offers good catalyst for use in the industry.

Examples

Next, examples and controls will be given to further explain the details of the invention.

Example 1:

Two hundred ml of 20 weight % aqueous solution of sodium hydroxide was prepared and it was heated to 80 °C. Next, 100 gm of a copper-nickel-zinc alloy (Cu, 5 weight %; Ni, 15 weight %; Zn, 80 weight %) was added to the solution slowly while watching the amount of hydrogen formed, then it was agitated for five hours for the development.

The treated alloy was filtered and washed in water till pH became close to 7. It was then wind (air) dried which gave 32 gm of the treated alloy. This alloy contained 16 weight % Cu, 48 weight % Ni and 38 weight % Zn. To this alloy 0.6 gm of graphite was added and by punching catalyst precursor tablets were made. Ten ml of this catalyst precursor was used to fill in a quartz glass tube reactor. As the reducing gas a mixture of $H_2/N_2=1:9$ (molar ratio) was introduced at the rate of 1000 hr^{-1} (LHSV) and reduction was done for five hours after the temperature was gradually raised to 400 °C.

Next, methanol (reagent grade) was introduced into the tube reactor at the rate of 6 hr^{-1} . Catalyst was evaluated at different temperatures. Methanol conversion and yield distributions of products were determined. Results are shown in Table 1.

Table 1

	Temperature (°C)	Conversion (%)	Product distribution (Mole %)					
			H_2	CO	CO_2	CH_4	DMH	Methyl formate
Exempl 1	299	68.62	67.05	32.51	0.37	0.07	---	---
	326	96.62	67.39	32.56	0.03	0.02	---	---
Control 1	303	37.90	67.72	31.60	0.09	0.05	0.02	0.52
	328	67.30	67.01	32.45	0.33	0.09	0.01	0.09
	359	91.49	66.98	32.71	0.24	0.09	0.02	0.02
	405	99.60	66.86	32.86	0.12	0.13	0.03	0.01

DME: Dimethylether.

Control 1:

108.7 gm of copper nitrate (trihydrate), 174.5 gm of nickel nitrate (hexahydrate) and 133.5 gm of zinc nitrate (hexahydrate) were dissolved in 1.5 liter of water. Separately 1.5 liter of the aqueous solution of anhydrous sodium carbonate (containing 265 gm of Na_2CO_3) was prepared. Both solutions were heated to 80 °C. Next, these solutions were quickly mixed and after completion of precipitation it was cured. After filtration and water wash 202 gm of precipitate was obtained. The precipitate was air-dried at 120 °C for about 12 hours and baked at 450 °C for two hours to make 135 gm of product. 2.7 gm of graphite was then added and a punching mold was used to make the catalyst precursor. Composition of the resultant precursor was Cu:Ni:Zn= 3:4:3 (atom ratio).

Next, 10 ml of this catalyst precursor was used to fill a quartz glass reactor. As the re-

ducing gas a mixture of hydrogen and nitrogen (1:9 molar ratio) was introduced at the rate of 1000 hr^{-1} (LHSV). Temperature was gradually raised to 400°C and the reduction was carried for five hours to make the catalyst.

Next, methanol was introduced into the reactor at the rate of 6 hr^{-1} (LHSV) and methanol conversion and the distributions of each product at different temperature were determined. Results are listed in Table 1. It is clear from the table that the methnaol conversion was low and in addition to methane methylformate and dimethylether were found.